Geophysical Monitoring of Cr(VI) Bioreduction at the Hanford 100H Site

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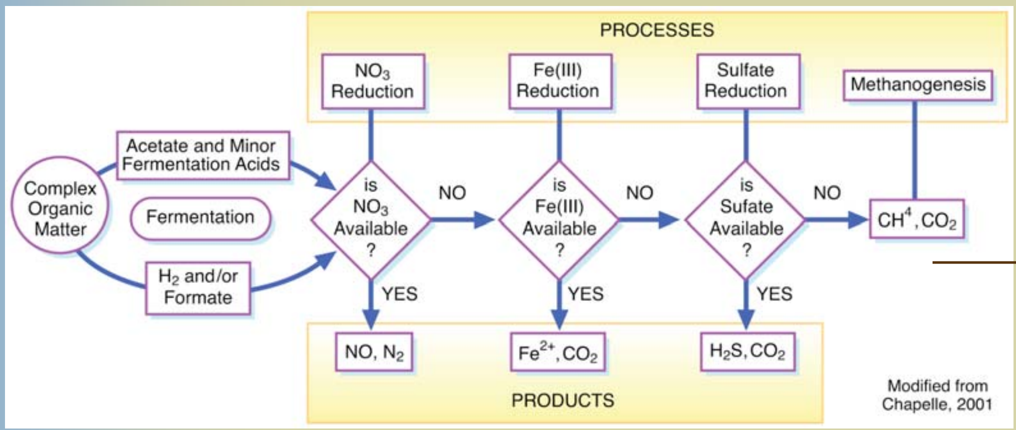
Outline

- Laboratory and Field Investigations - Exploring the use of Geophysical Data for:
  1. Hydrogeological Characterization
  2. Geochemical Monitoring
     - Amendment Distribution
     - System Transformations
- Comparison of geophysical results with geochemical measurements and modeling
- Role of heterogeneity



Can Time Lapse Geophysical Methods be used to detect HRC distribution and products?

Components or Products that could influence geophysical signatures:

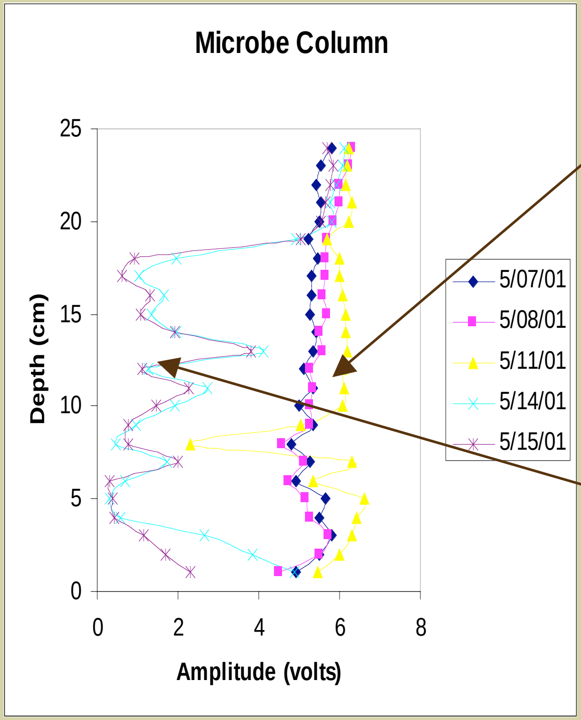
- HRC
- Gases (N_2, CO_2)
- Mineralogy (Chromium ppts, FeS, FeII clays, elemental sulfur, white precipitates)
- Solutes (Bromide, NO_3, SO_4, $HCO_{3,}$)

Procedure:

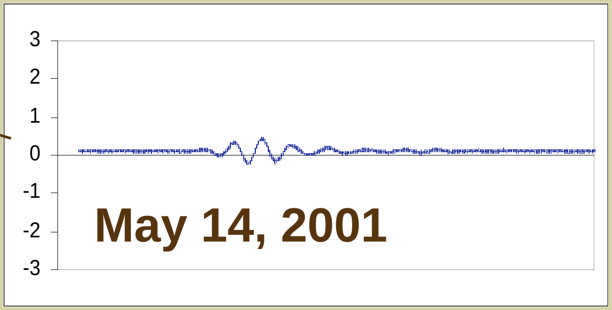
- Lab studies
- Field Scale imaging
- Comparison with geochemical measurements and modeling

Laboratory Measurements of System Transformations: **Gasses**

Column
Laboratory
Experiments
Electron
Acceptor:
Nitrate;
Carbon
Source:
Acetate

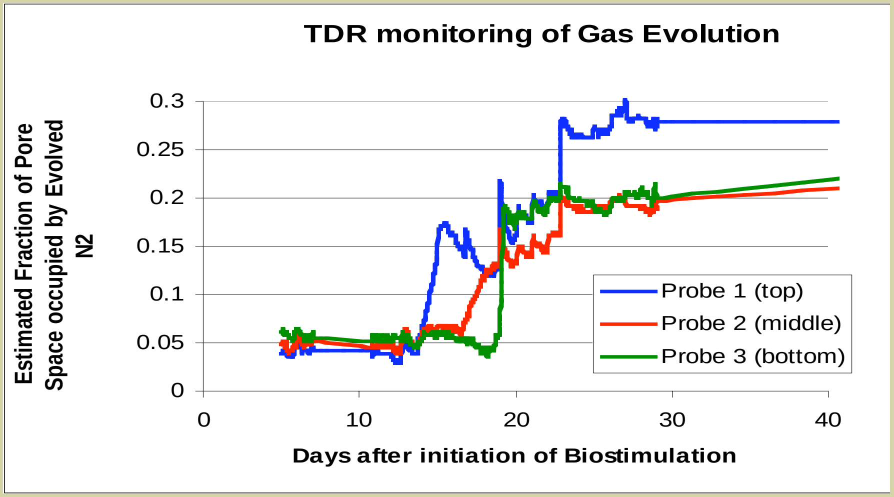


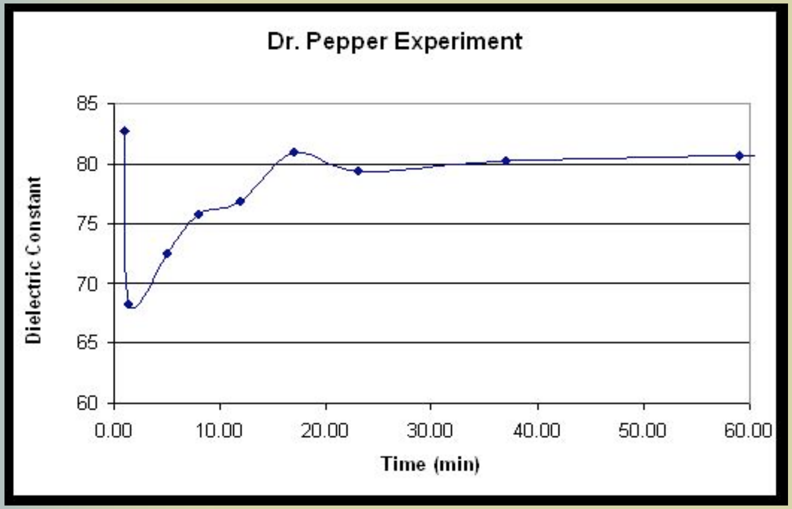
Seismic Signal at 8cm down column length



Seismic amplitudes severely attenuated as gasses form

Radar signatures of Evolved Gas

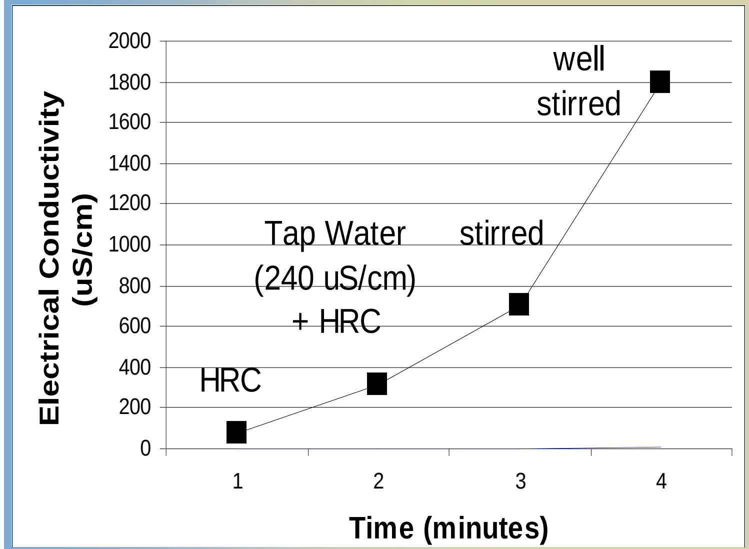


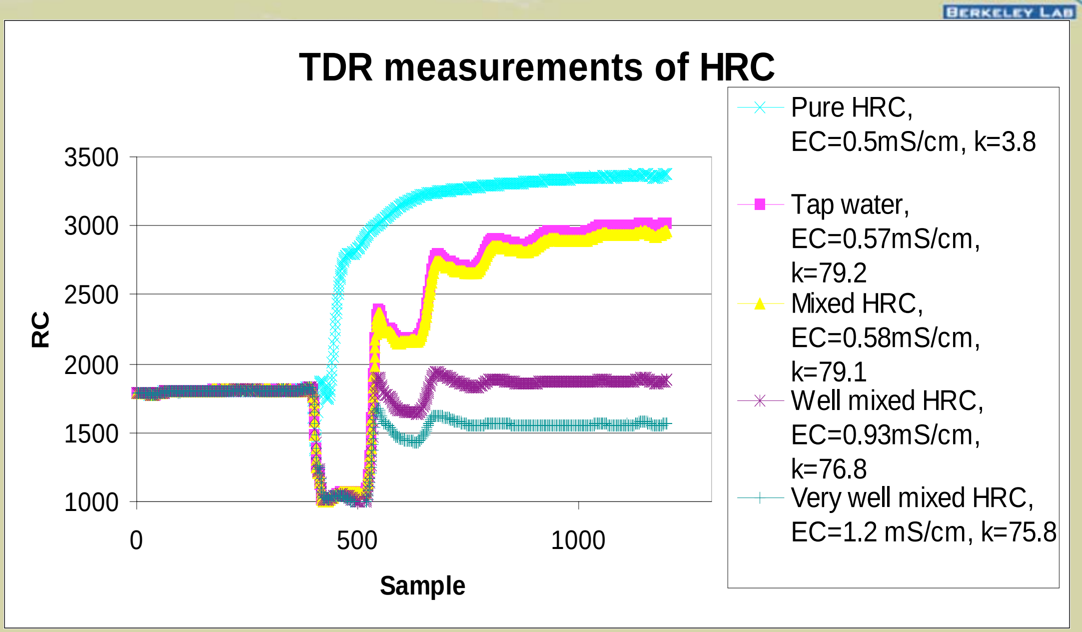


Radar travel times change in a predictable way as gas is evolved in a system

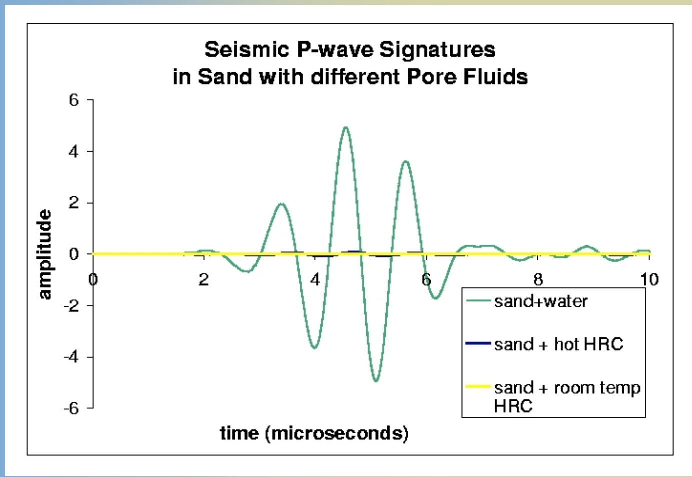
- Velocity increases
- Dielectric constant decreases

Geophysical Measurements of HRC





Comparison of EC and TDR suggests that radar amplitudes can be used to estimate EC

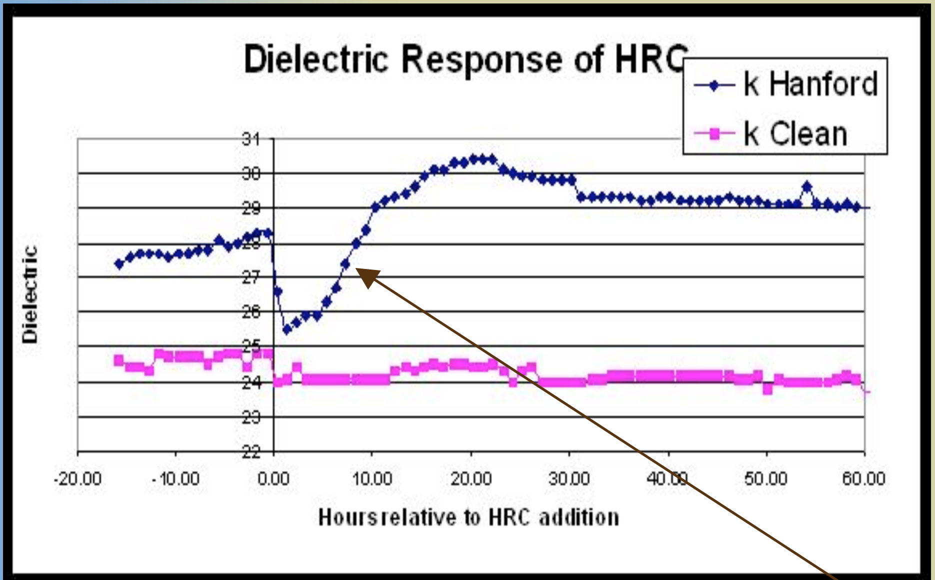


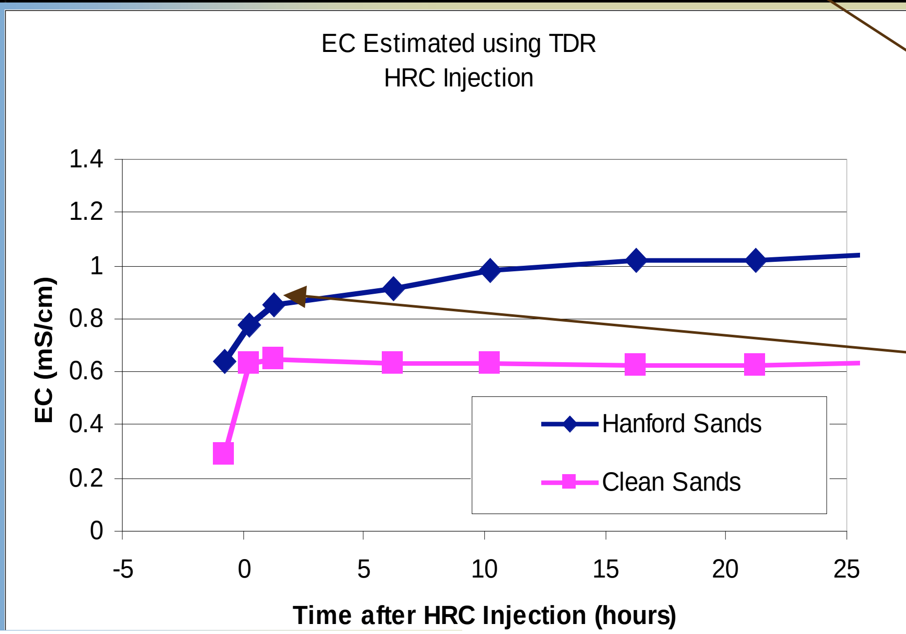
HRC:

- Initially electrically resistive. As it mixes with water, it becomes more electrically conductivity.

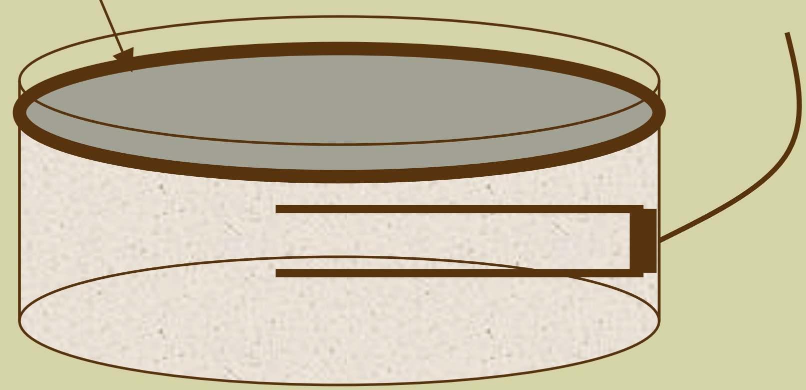
- Compared to water, the
  - Electrical conductivity is higher
  - Dielectric constant is lower
  - Radar attenuation is higher
  - Seismic response severally attenuated

HRC radar experiments in presence of Sediments



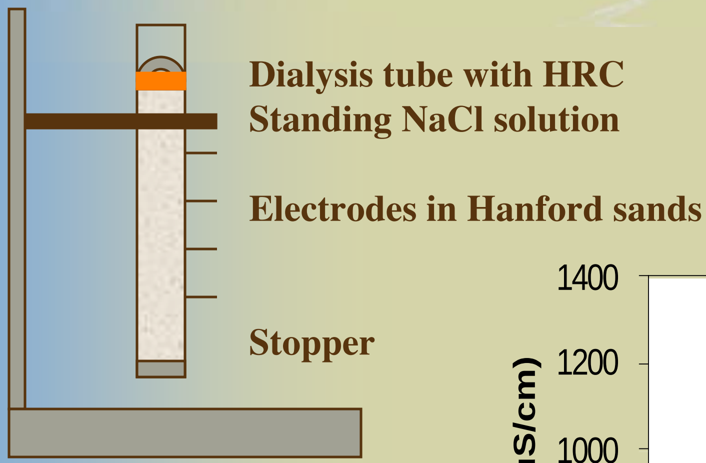


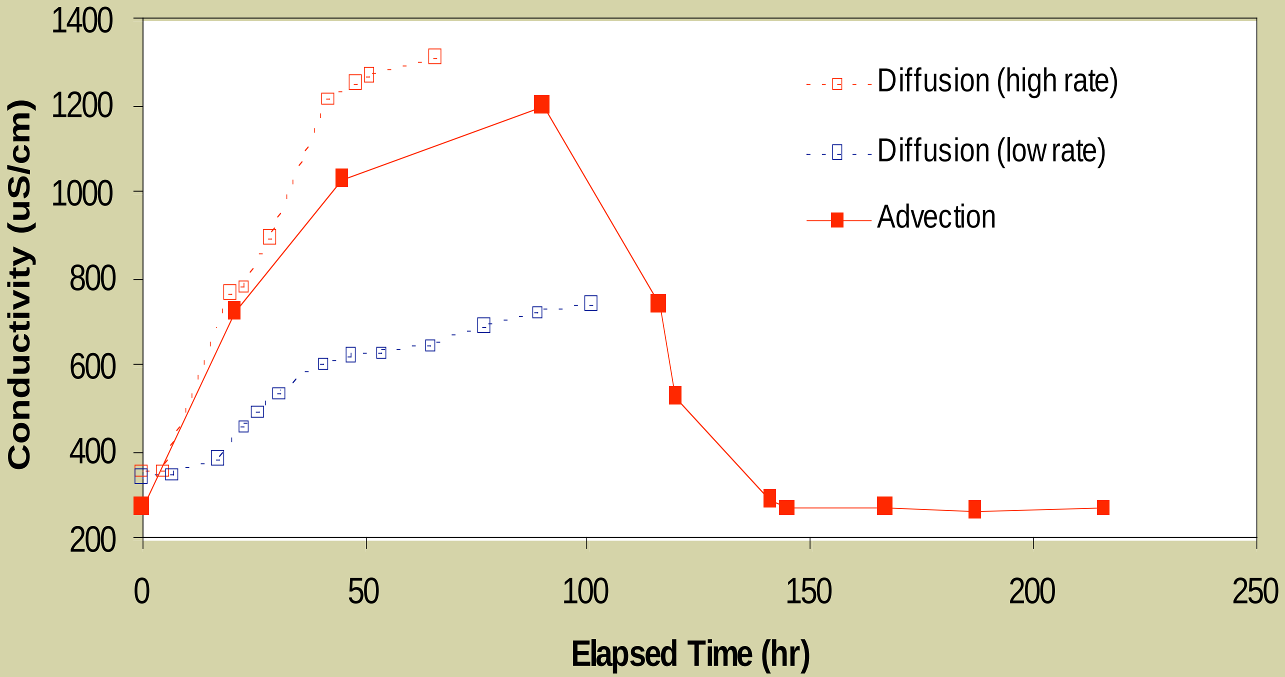
HRC added to saturated sediments



- Hanford sand more ‘reactive’ than clean sand;
- Hanford dielectric decreased more **initially** and then rebounded to higher than initial values at **longer times**;
- Increase in electrical conductivity in Hanford sands mollified by slight decreased caused by gasses.

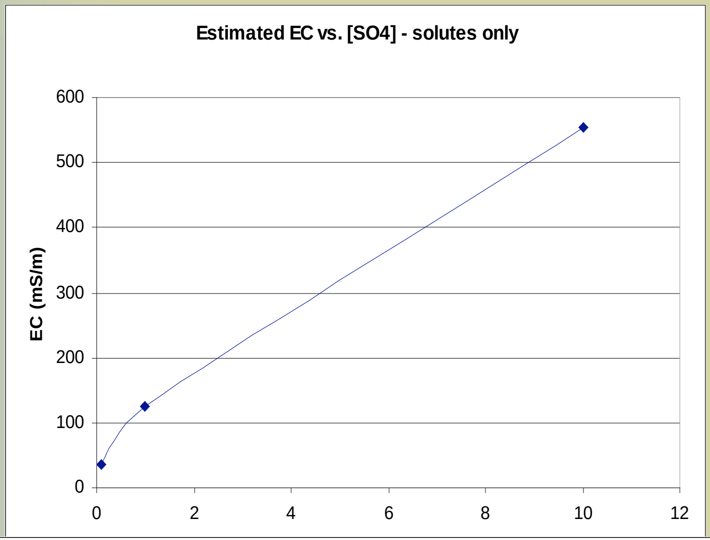
HRC electrical experiments in presence of Sediments

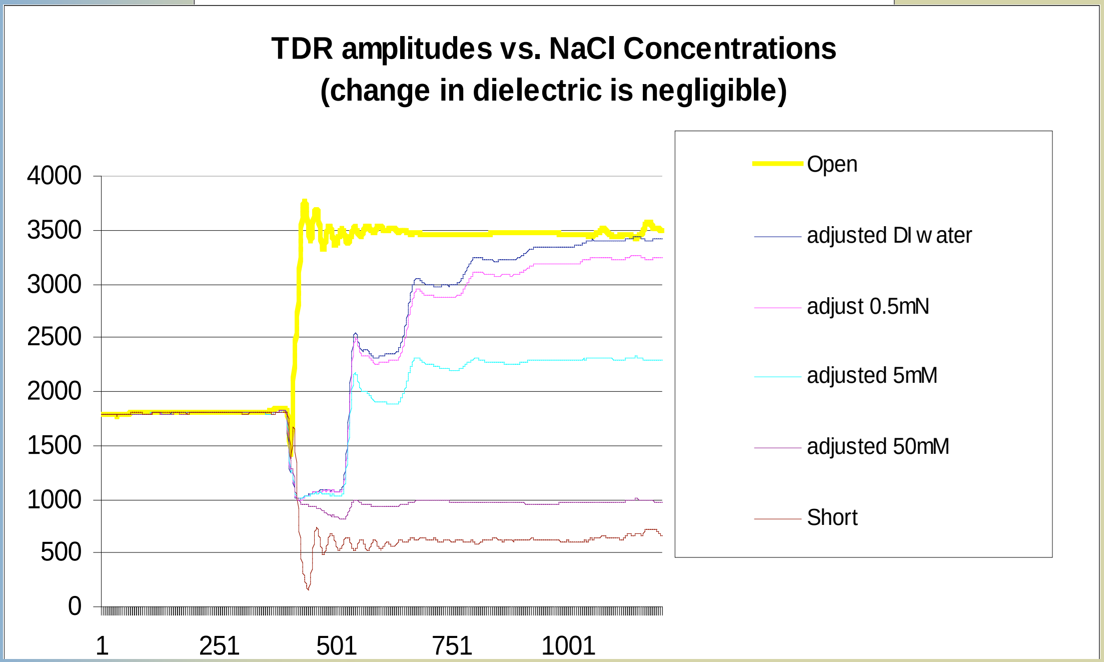




If the the majority of the pores were not isolated by gas bubbles bridging pore throats, the electrical conductivity increased but then returned to 'baseline' after plume passed through measurement zone

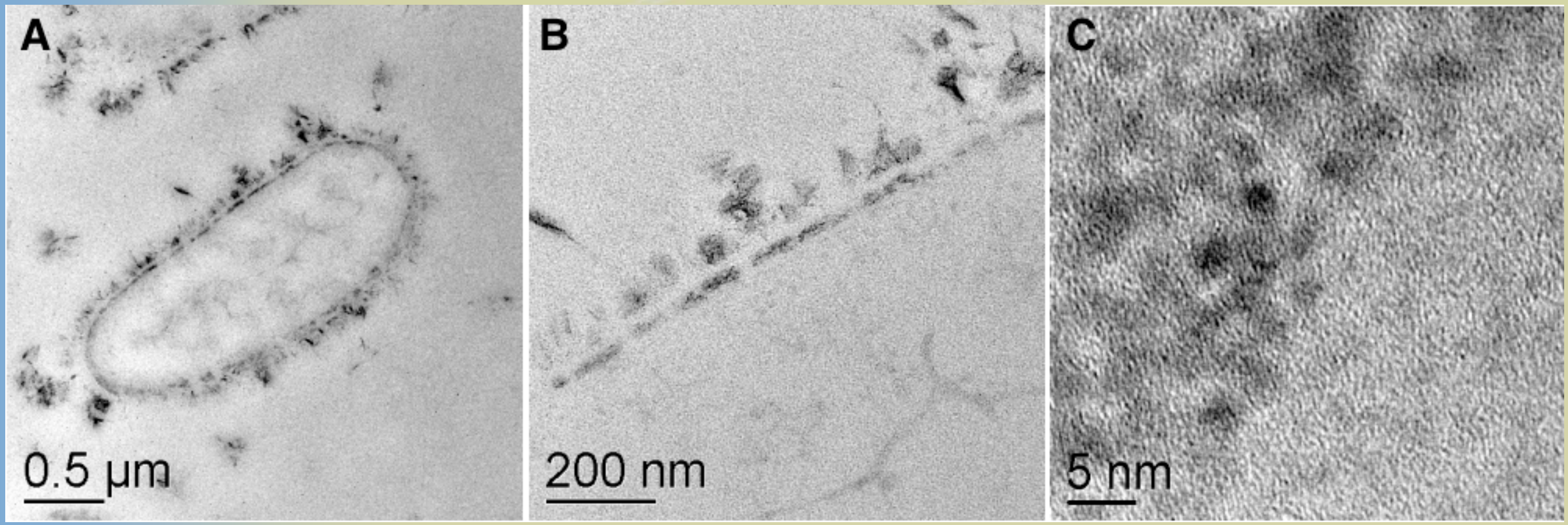
Geophysical Responses to Solutes

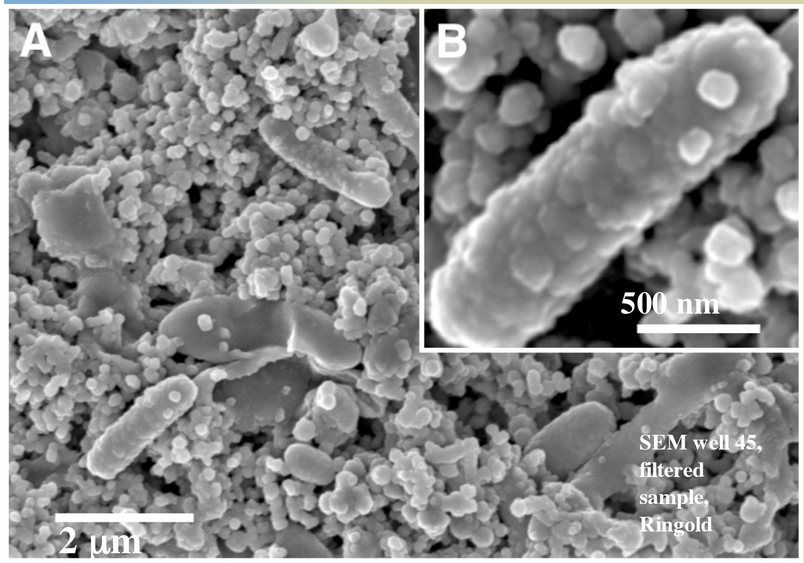




- •Electrical Conductivity Increases;
- •Radar attenuation Increases;
- •Seismic not affected

Nature of 100H FeS Precipitates

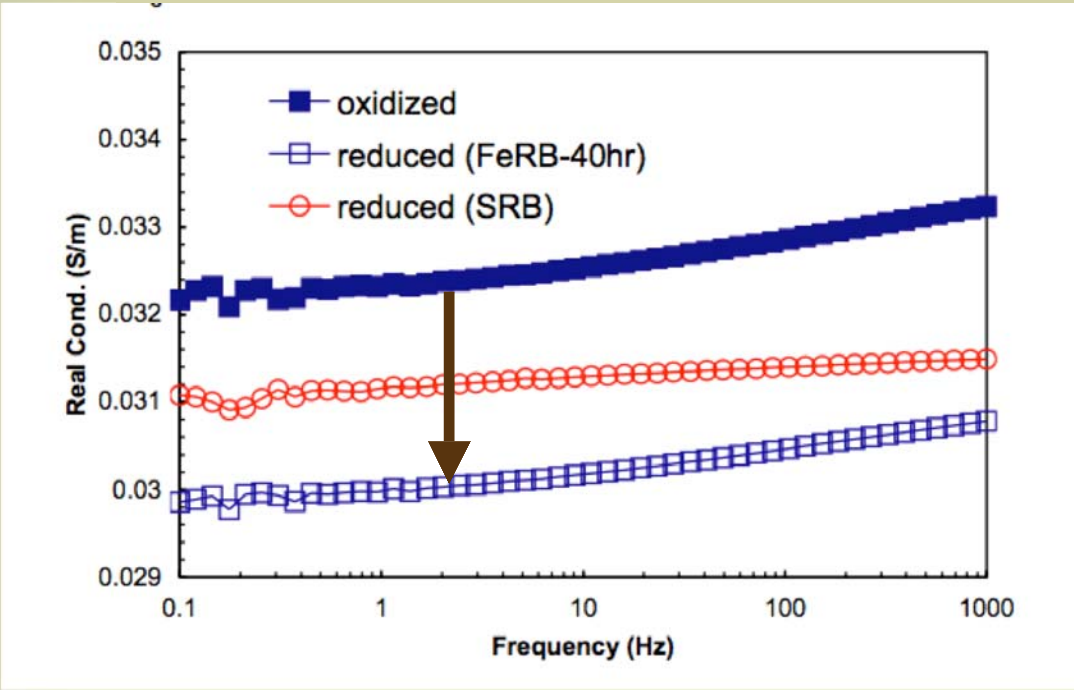




- **FeS Precipitates**
  - Recovered from fluid samples and sediments (Ringold)
  - Nanoparticulate aggregates closely associated with cell surfaces and polymers

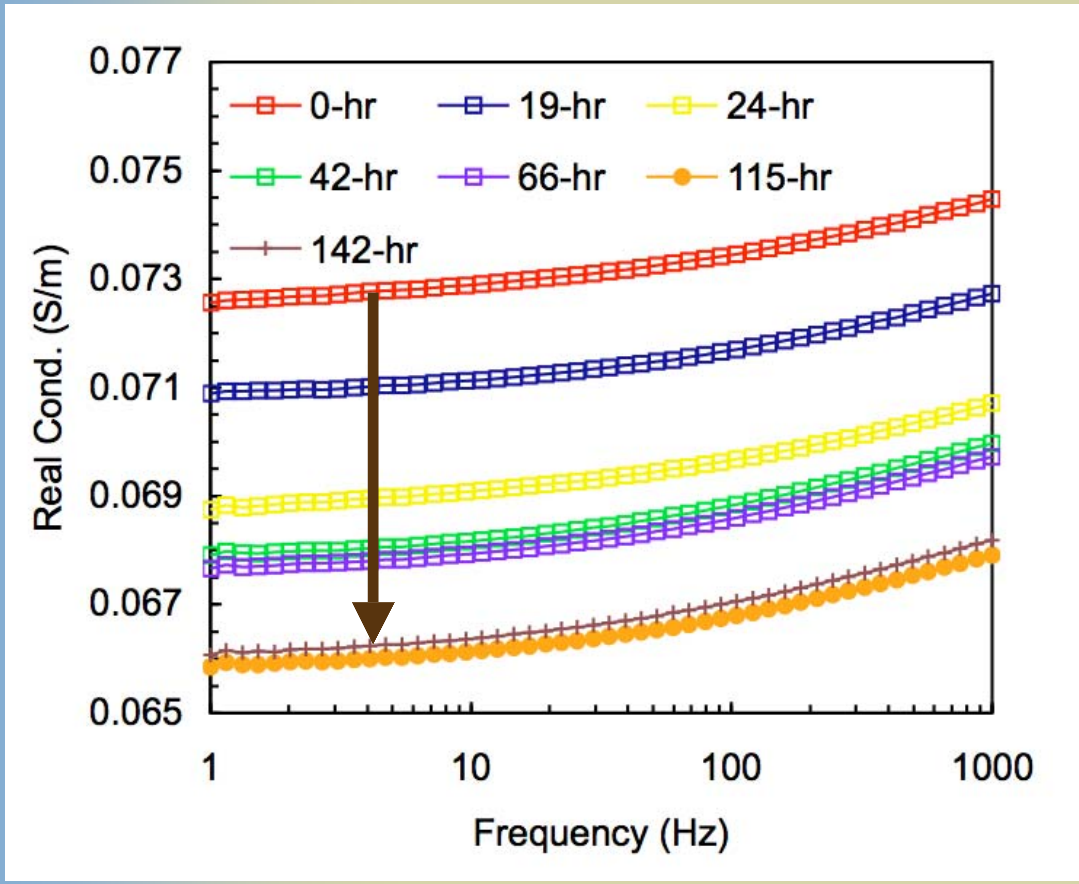
TEM upper images and SEM lower image (non-filtered samples)

Electrical Conductivity Response to Change in Mineralogy



EC decreases as iron and sulfate are reduced by ~ 1 to 2 s-m
Dissiminated FeS, clay collapse

Electrical Signature of Elemental Sulfur Production



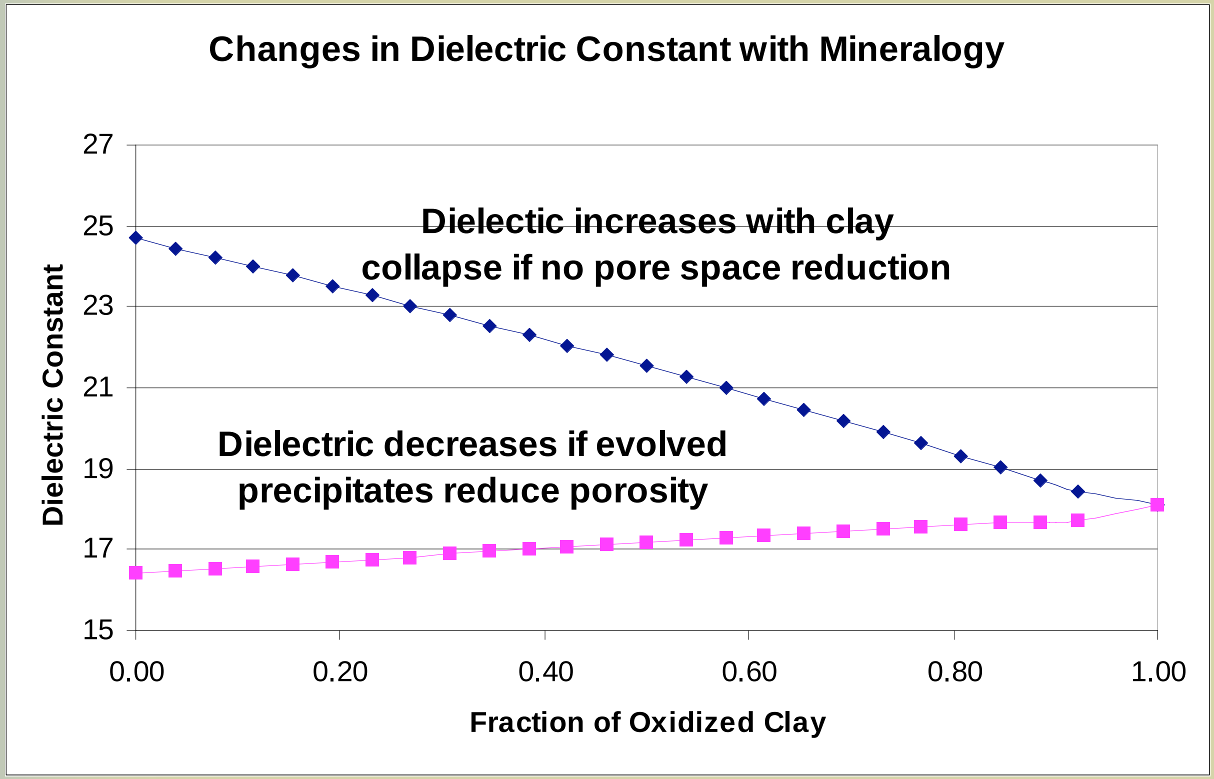
Sulfide reoxidation: Electrical monitoring of sulfide oxidation of Rifle Sediment saturated with sulfide-rich groundwater

Becomes grey upon exposure to HS- (Fe reduction). Resistive elemental sulfur ppt in pore space

Electrical conductivity reduced by ~7 mS/m

From Sulfate Reduction:

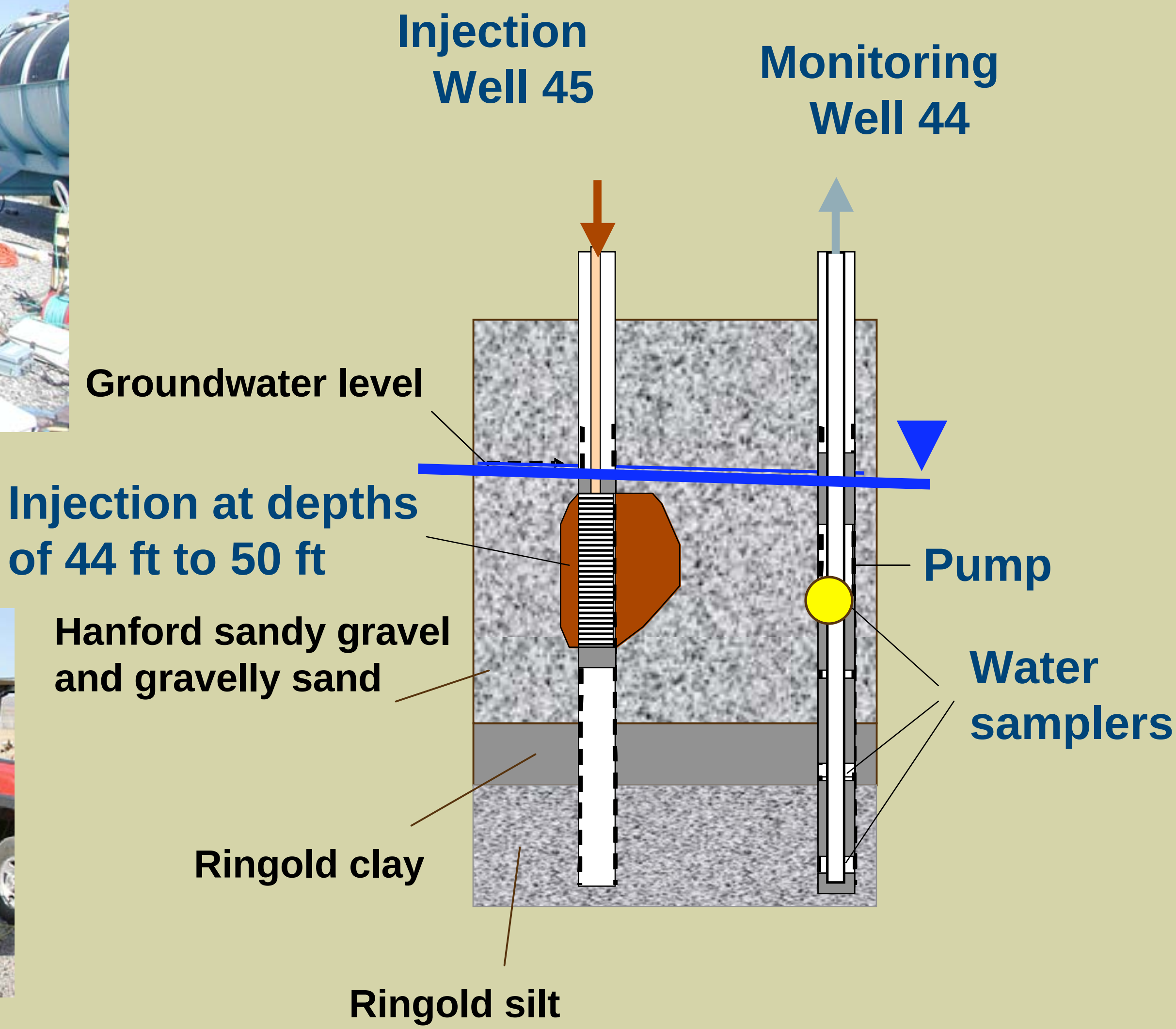
Dielectric response to change in clay type and formation of precipitates

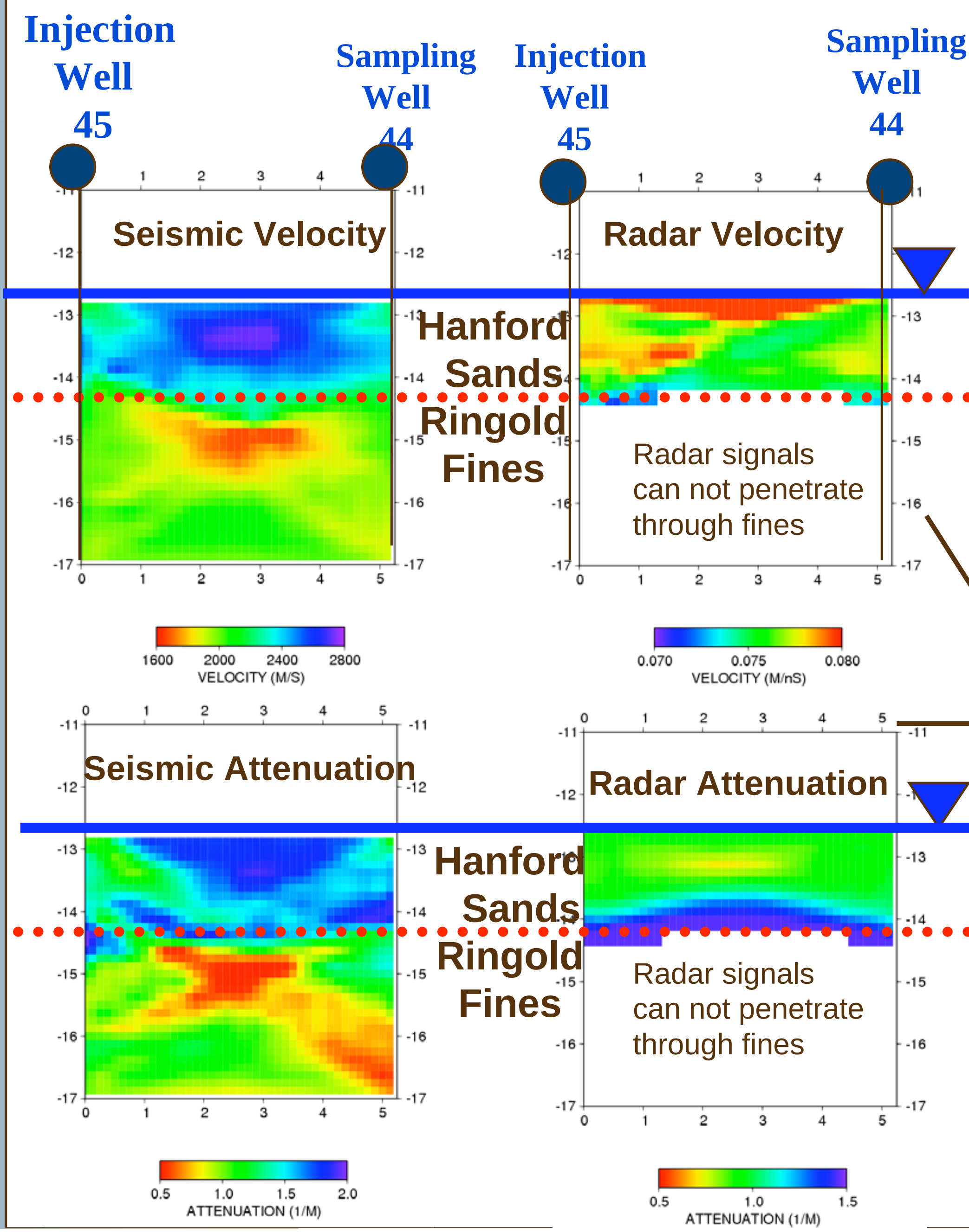


Change in clay type/structure could increase dielectric constant by 2 if no change in porosity.

If evolved precipitates cause a reduction in porosity from 0.35 to 0.27, dielectric constant could decrease by 1.

Field Studies: Geophysical Characterization and Monitoring associated with HRC Injection Test



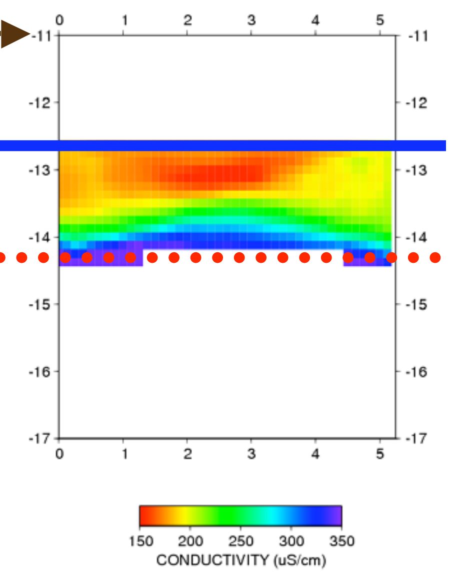


Groundwater Flow

- ***Delineation of Hanford and Ringold Fms***

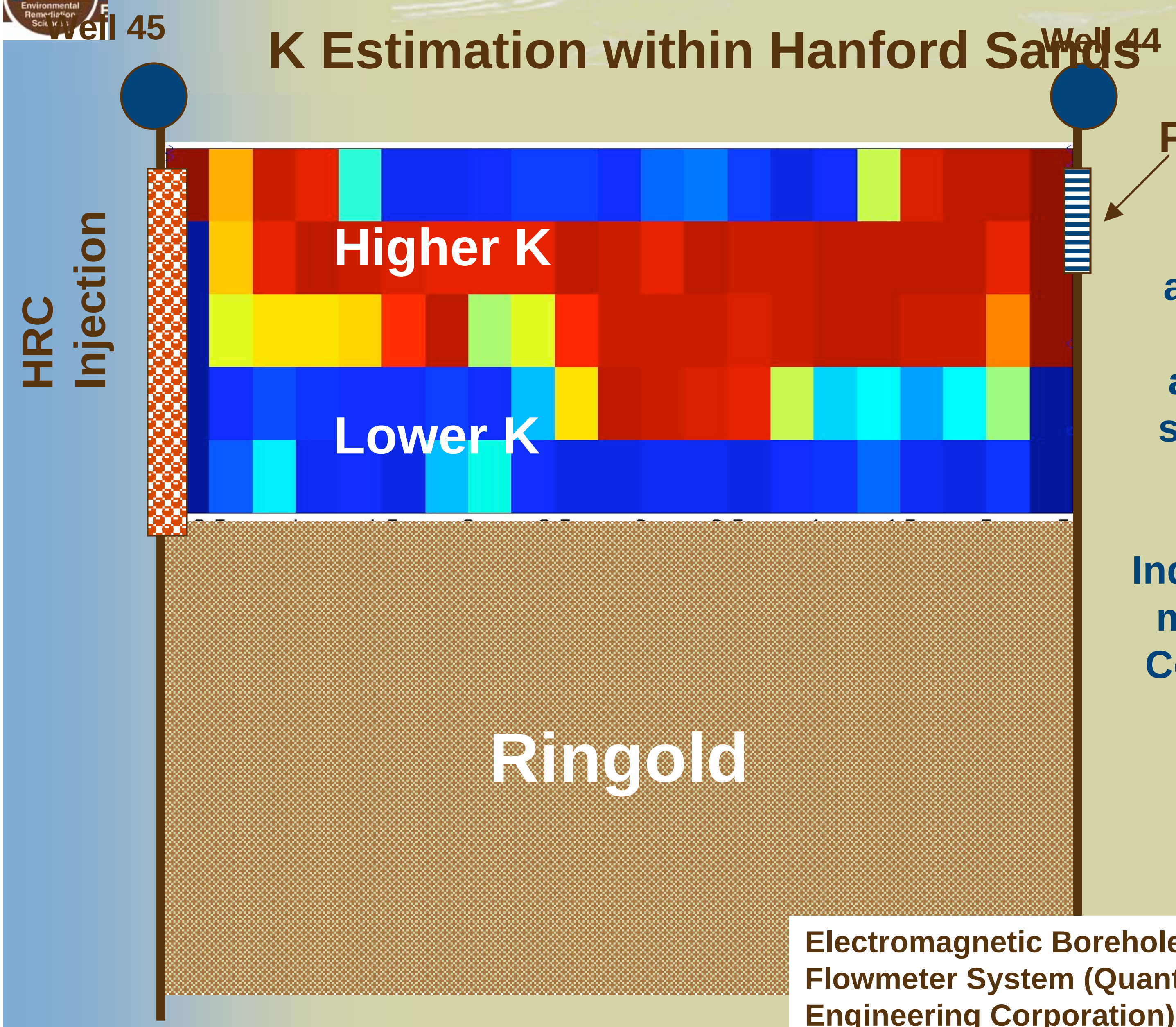
- ***Estimation of K variation within Hanford***

$$\sigma \approx \frac{\alpha[dB/m]\sqrt{\kappa}}{1.64}$$



K Estimation within Hanford Sands

Pumping



Discriminate analysis of radar velocity, radar attenuation, and sparse flowmeter data

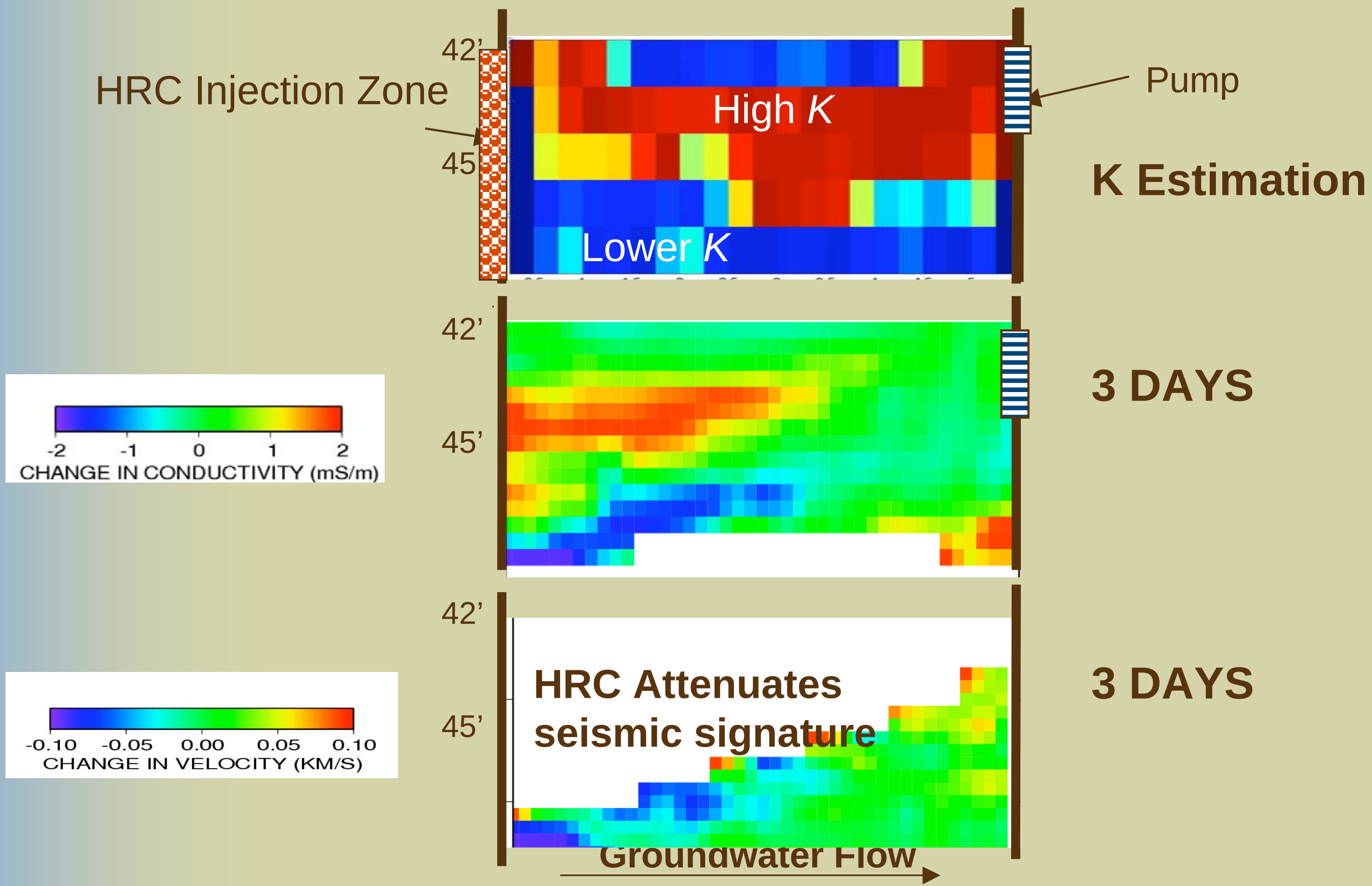
Indicator Cutoff :the median Hydraulic Conductivity value 10^{-3} cm/s

Electromagnetic Borehole Flowmeter System (Quantum Engineering Corporation)

Experimental and Geophysical Monitoring Timeline

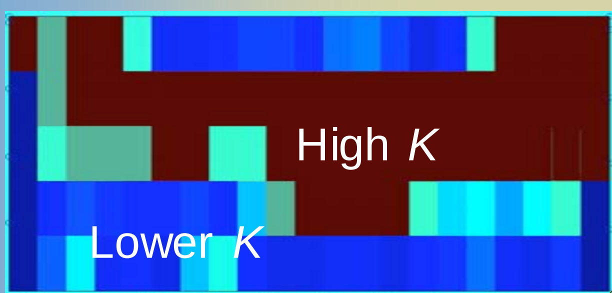
Date	Activity	Geophysical Rubric	Days past HRC Injection
7-Jul-04	Bromide Injection		-27
3-Aug-04	Seismic+Radar	Prior (BASE2A)	0
Aug3 (<1hr) 5PM	HRC Injection		0
4-Aug-04	Seismic	Post1A	1
5-Aug-04	Radar	Post 1A	2
5-Aug-04	Seismic	Post 2A	2
5-Aug-04	Bromide Injection		2
5-Aug-04	Pumping Starts		2
6-Aug-04	Radar	Post 2A	3
11-Aug-04	(bromide bt)		8
18-Aug-04	Seismic+Radar	Post 3A	15
Aug 16 - Aug 20	(microbial bt)		13-17
30-Aug-04	Puming Stops		27
2-Sep-04	Seismic+Radar	Post 4A	30
28-Oct-04	Seismic+Radar	Post 5A	86
1-Jun-05	Seismic+Radar	Post 6A	302
7-Jun-05	Bromide Injection		307
7-Jun-05	Pumping Starts		307
7-Jun-05	Seismic+Radar	BaseB	307
9-Jun-05	Seismic+Radar	Post1B	309
23-Jun-05	Seismic+Radar	Post2B	323
11-Jul-05	Pumping Stops		341
2-Aug-05	Radar	Post3B	363
30-Mar-06	Seismic+Radar	2006	603
10-Apr-06	Bromide Injection		614
10-Apr-06	Pumping Starts		614
2-May-06	Pumping Stops		636

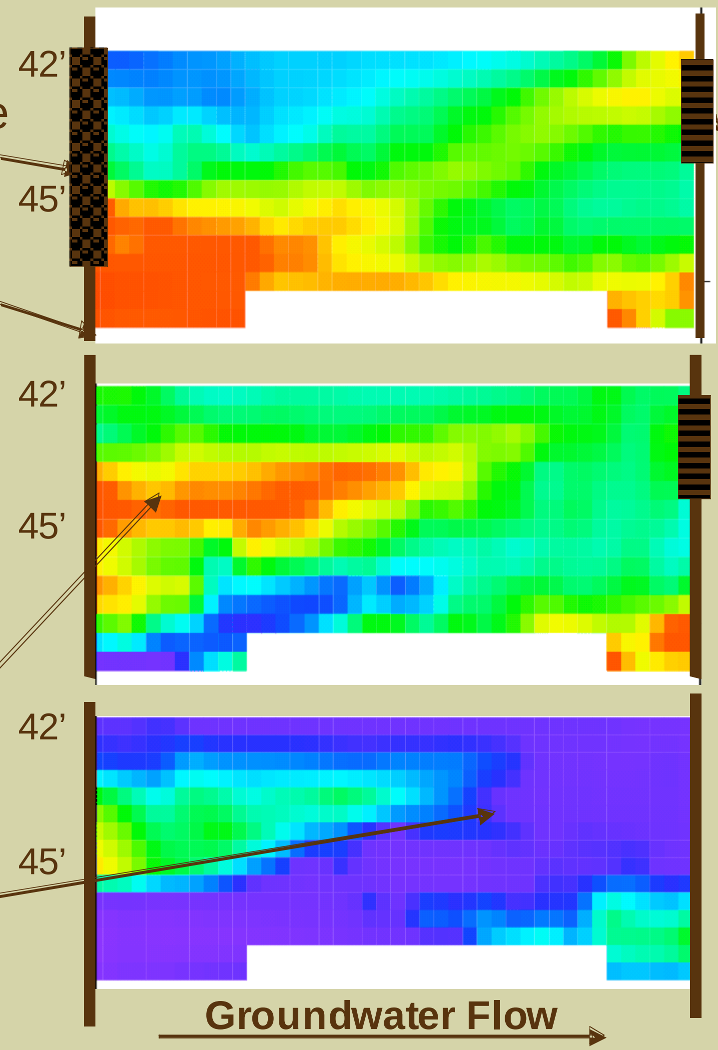
Early Signatures of HRC

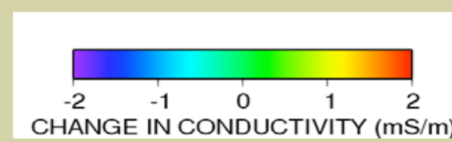


Post-HRC Injection Changes in Estimated Electrical Conductivity

$$\sigma[mS/m] \approx \frac{\alpha[dB/m]\sqrt{\kappa}}{1.64}$$





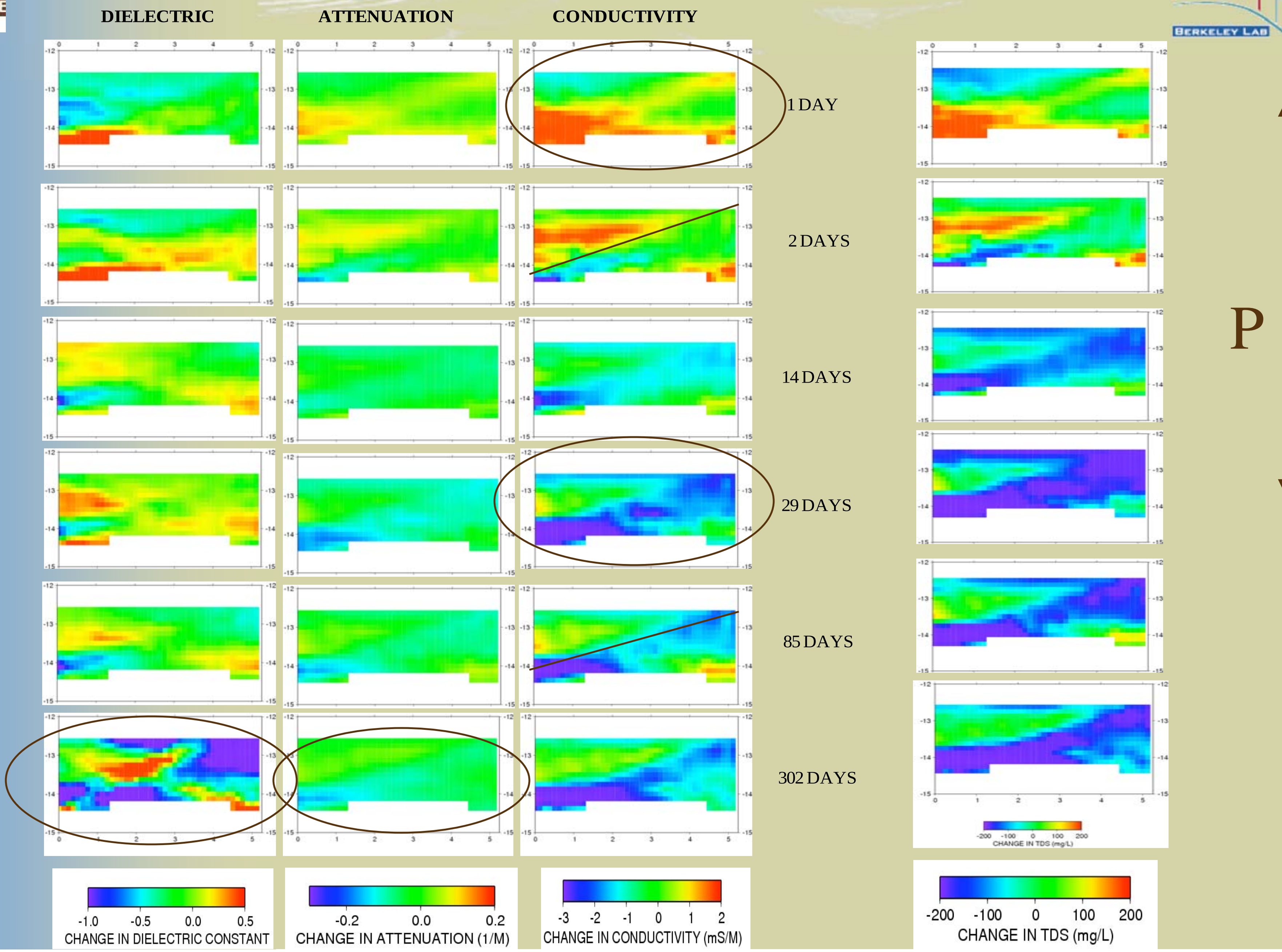


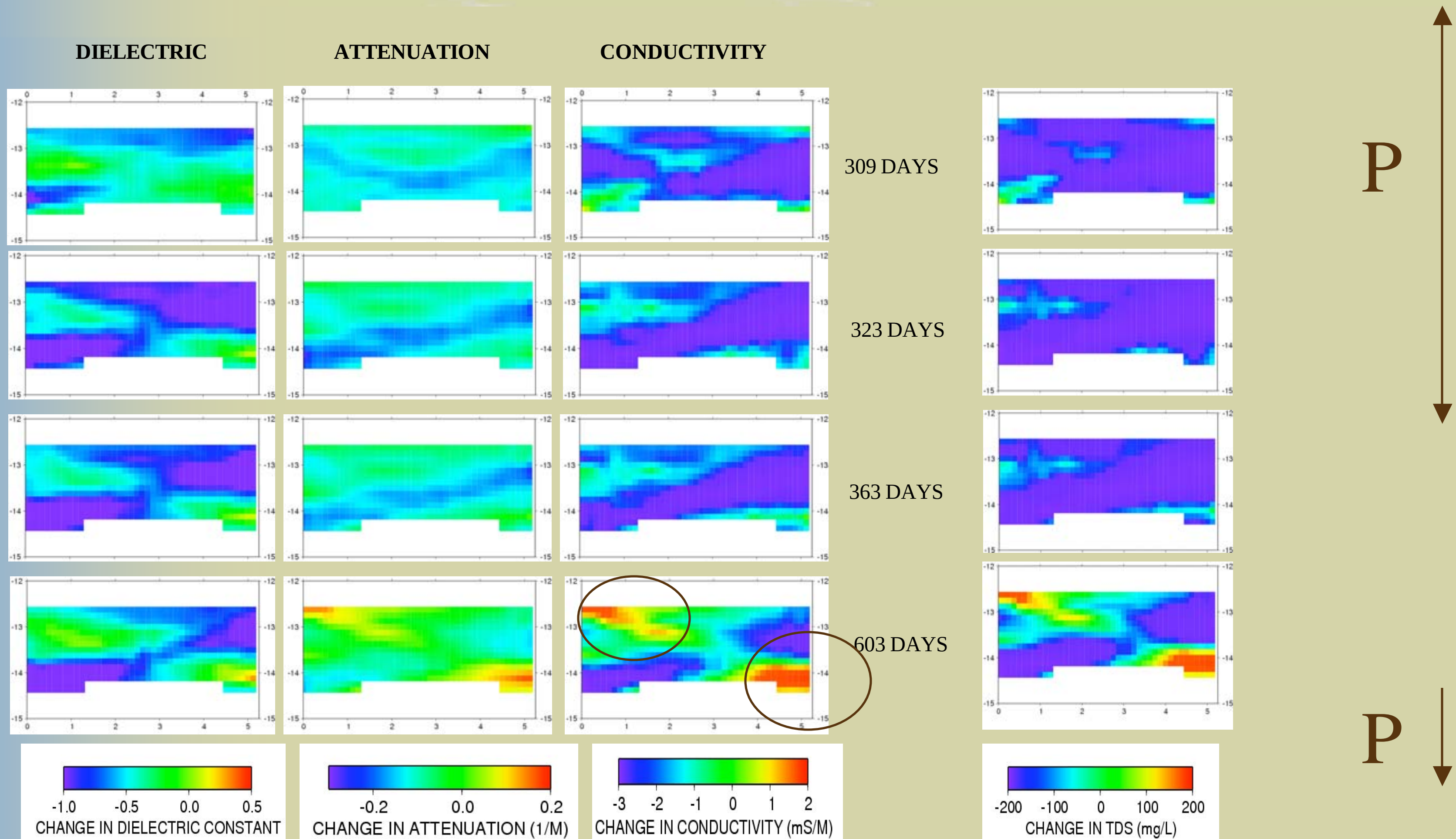
Hypothesis : H ions, Lactic acid

Hypothesis : Reaction halo **associated with change in TDS**

Up to 10% change

RADAR WELL PAIR 45 -44



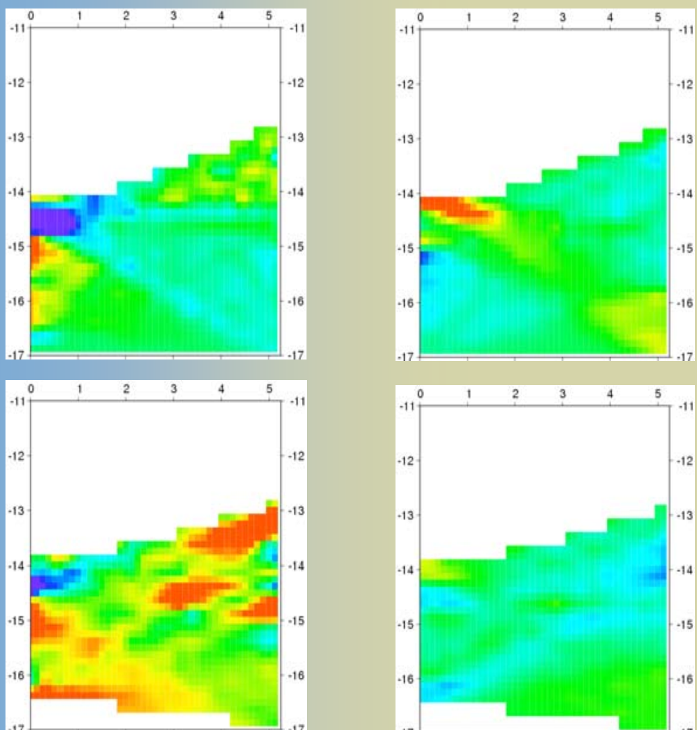


DIELECTRIC
ATTENUATION
CONDUCTIVITY
309 DAYS
323 DAYS
363 DAYS
603 DAYS
-1.0 -0.5 0.0 0.5
CHANGE IN DIELECTRIC CONSTANT
-0.2 0.0 0.2
CHANGE IN ATTENUATION (1/M)
-3 -2 -1 0 1 2
CHANGE IN CONDUCTIVITY (mS/M)
-200 -100 0 100 200
CHANGE IN TDS (mg/L)
P
P

SEISMIC WELL PAIR 45 -44

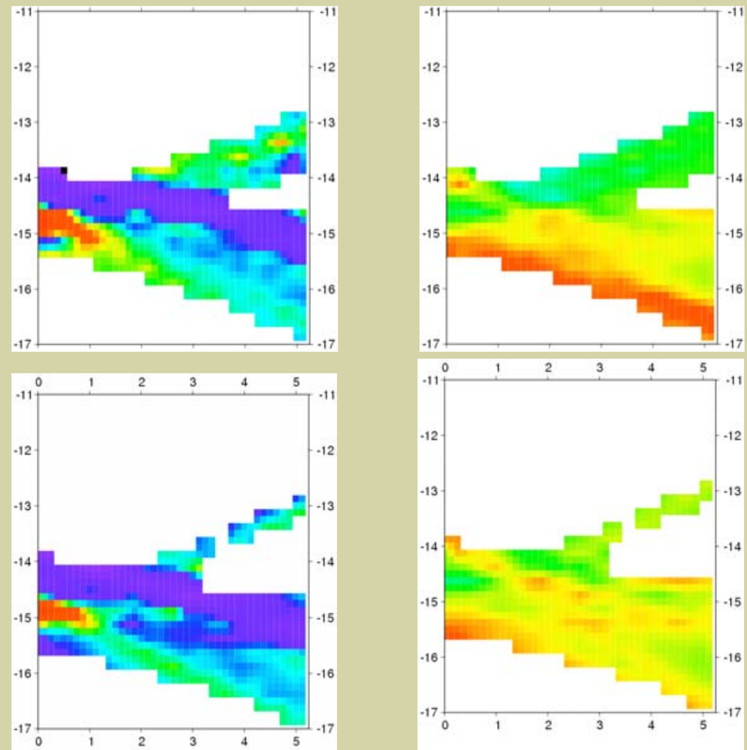
VELOCITY

ATTENUATION



1 DAY

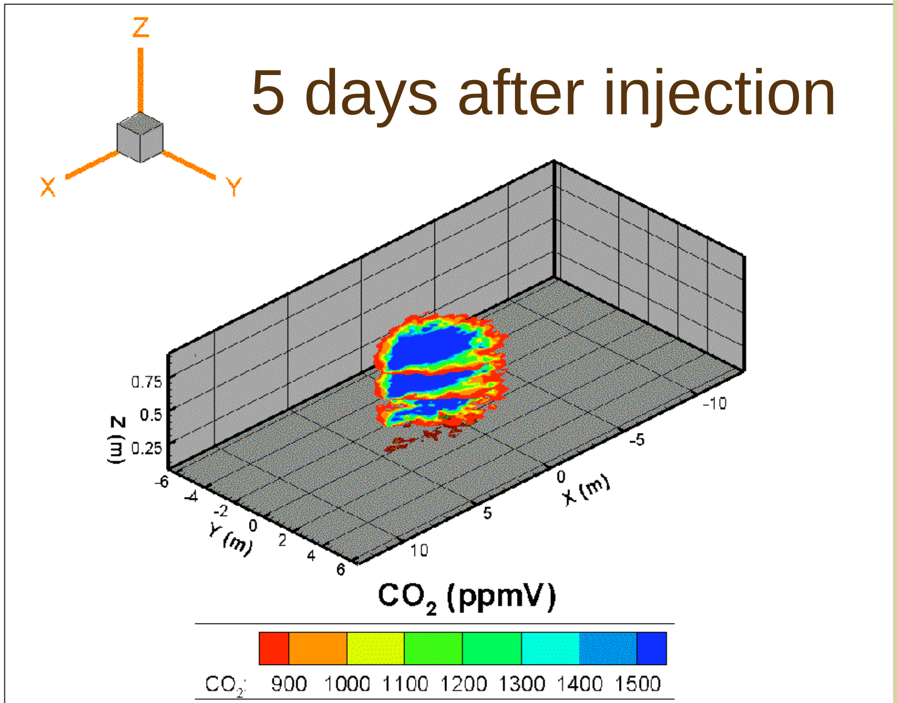
85 DAYS

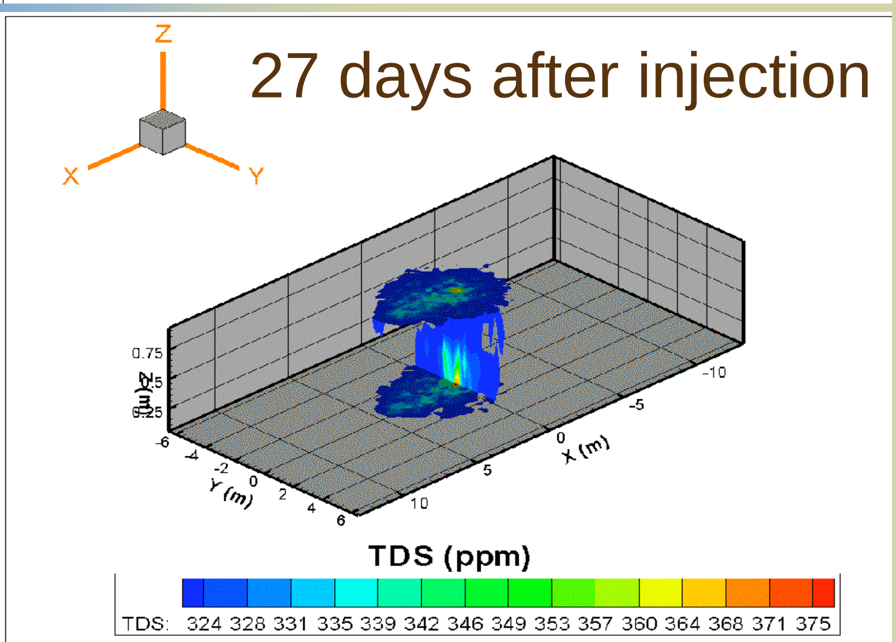


302 DAYS

323 DAYS

Comparison with Modeling and Geochemical Measurements





TOUGH3D Modeling
(Sumit and Eric)

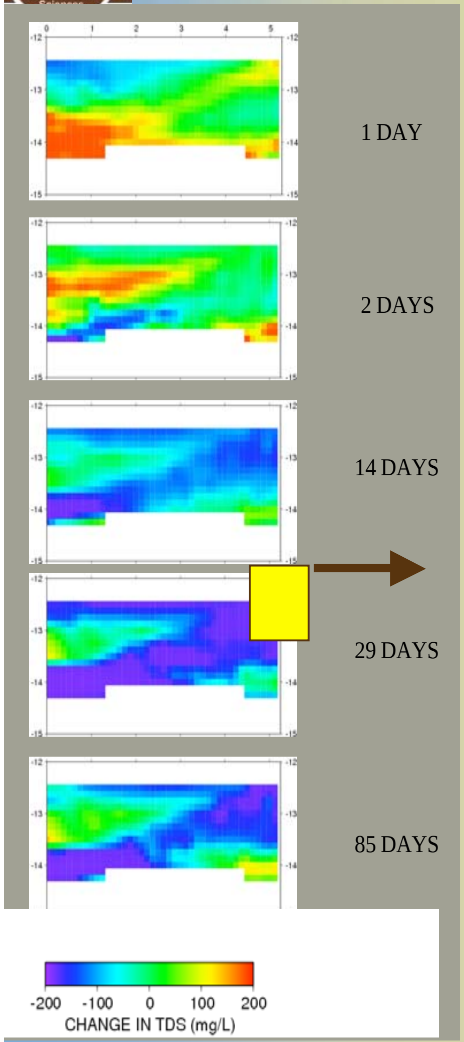
The primary mineral-water interaction that occurs over the period of the injection test involves the dissolution of calcite:

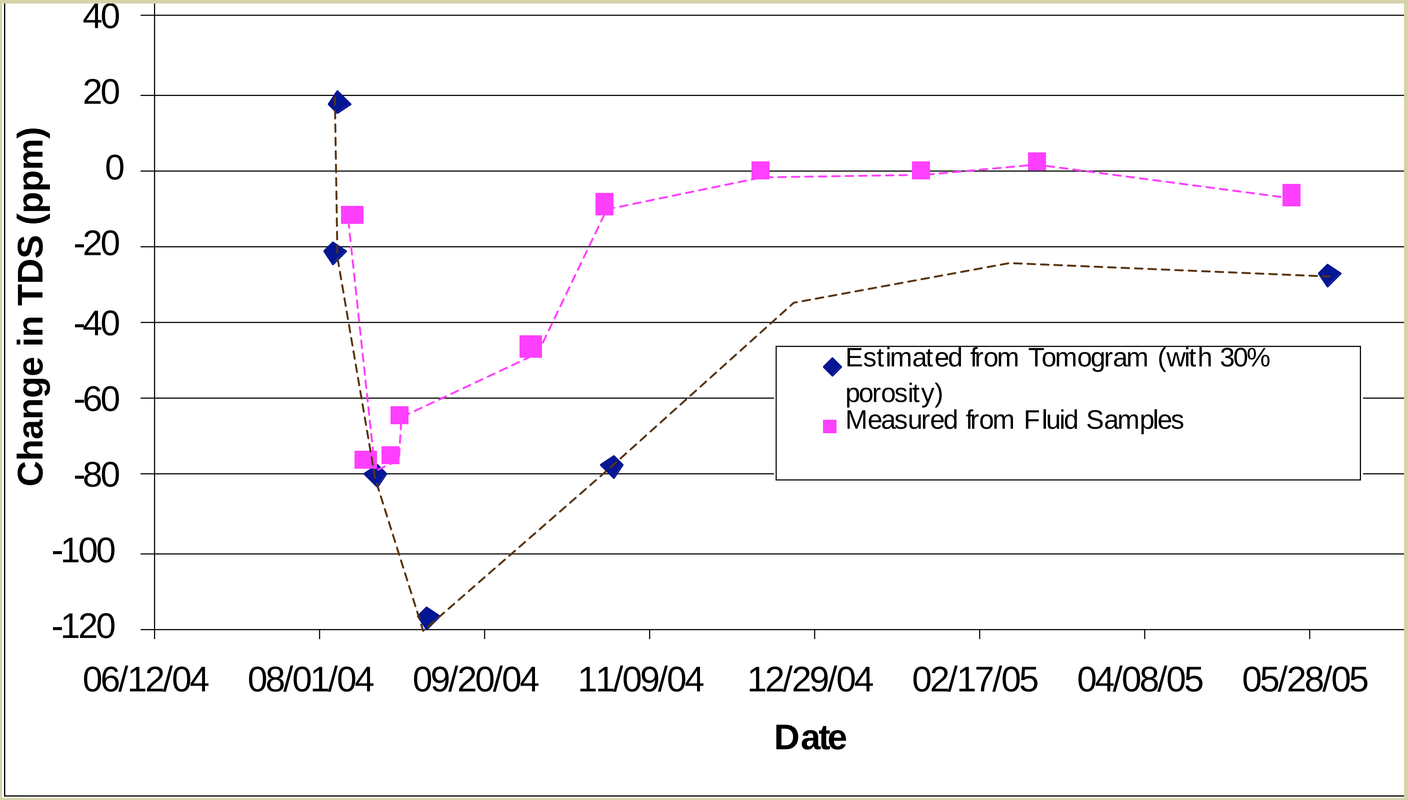
$H^+ + CaCO_3 = Ca^{2+} + HCO_3^-$

CO2 remains in dissolved phase.

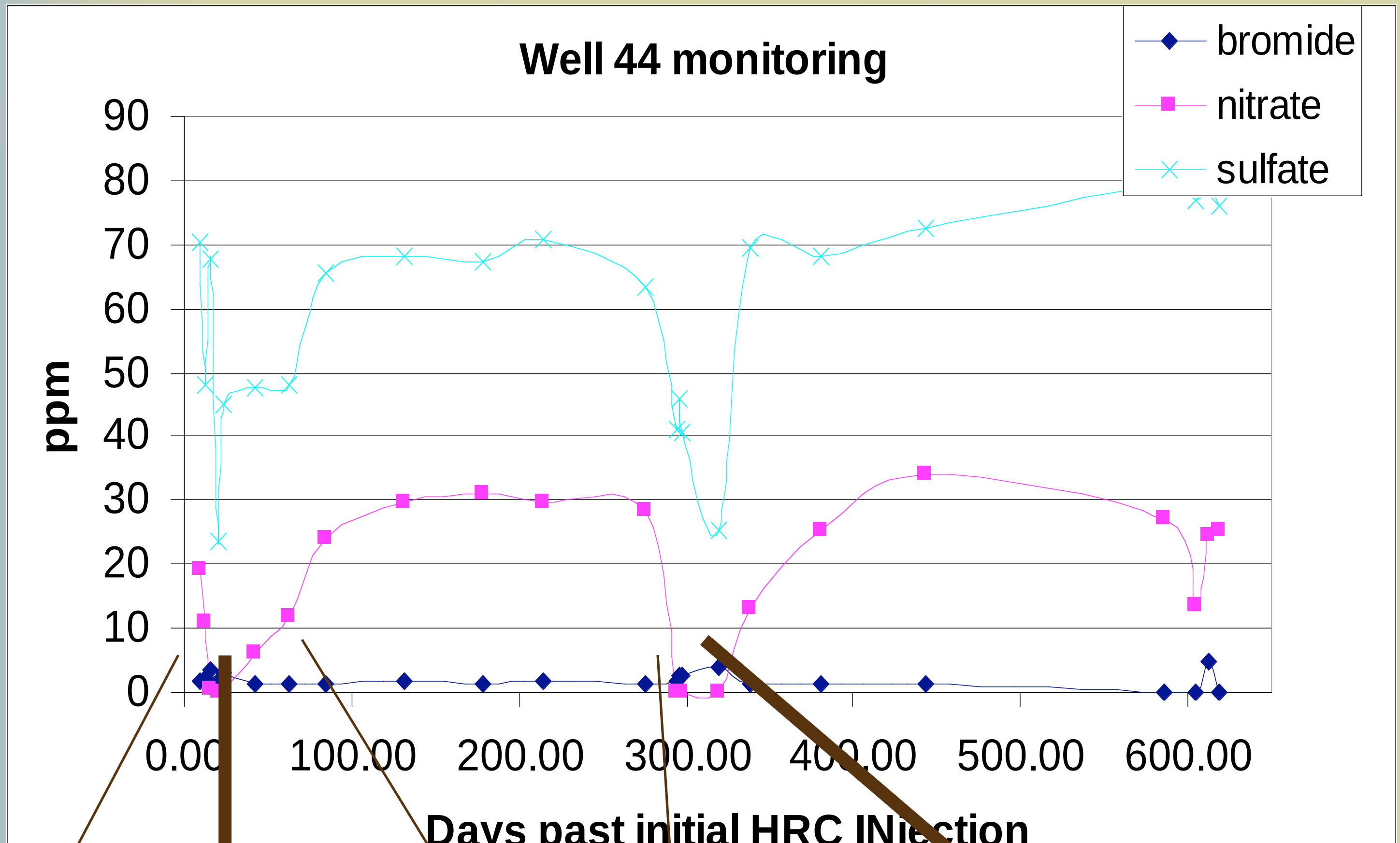
TDS increases near injection zone

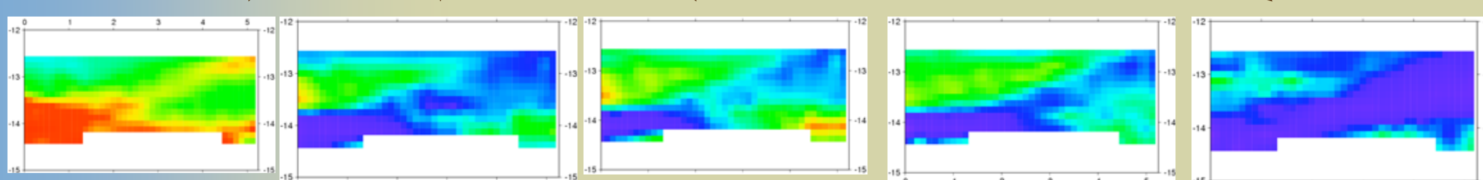
Comparison of Geophysical and Geochemical Data





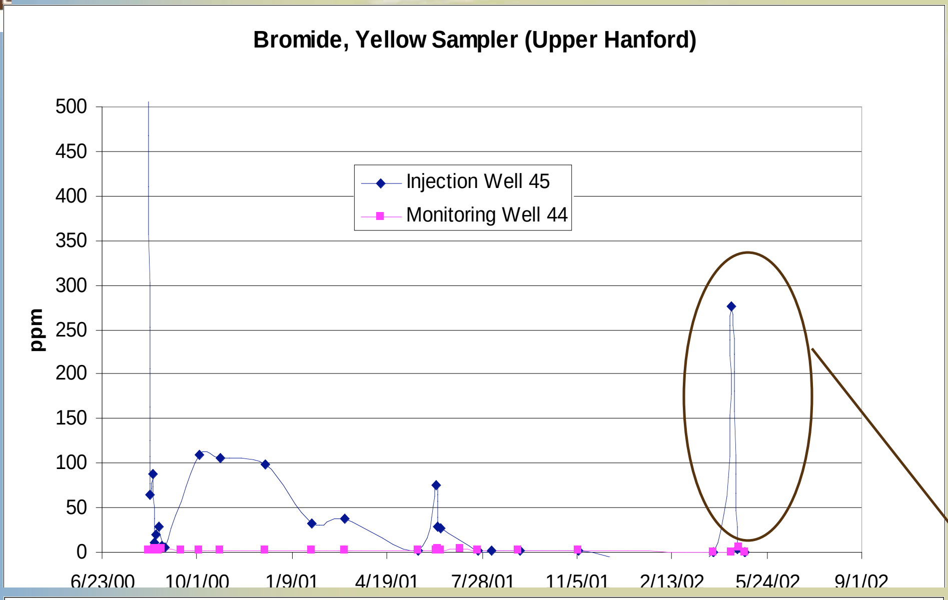
Comparison of Change in measured TDS (Sulfate and Nitrate only - Mark) and Topographically-estimated TDS at Downgradient Yellow Sampler

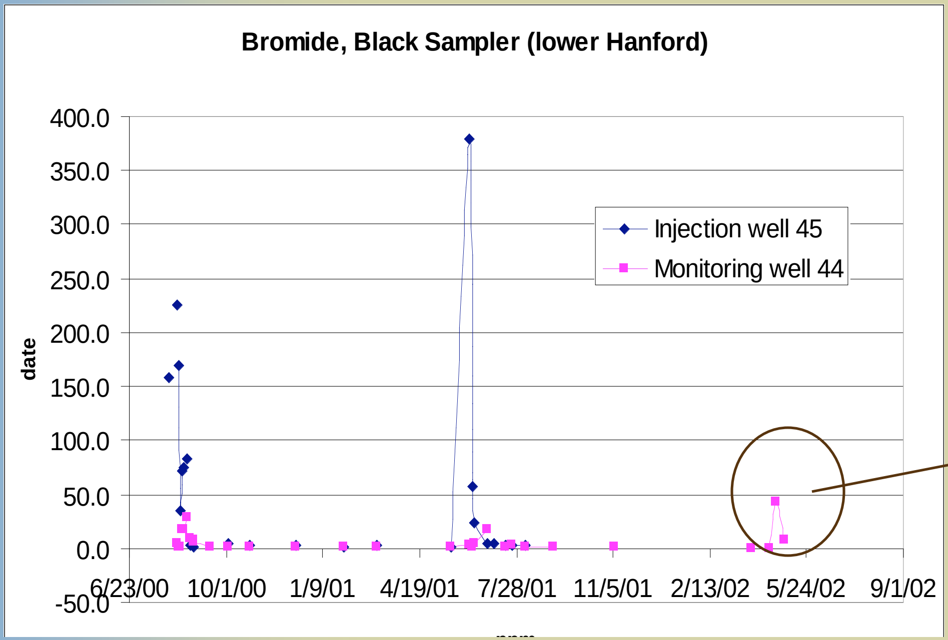




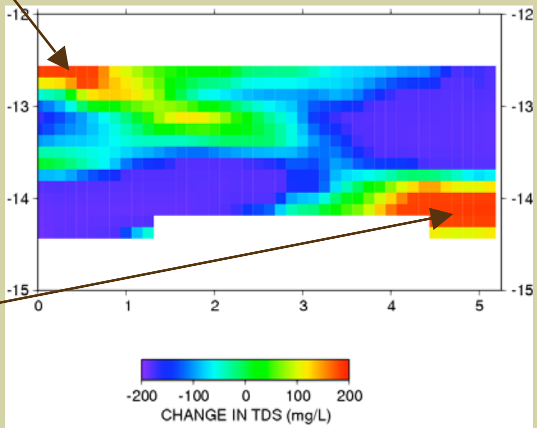
Decrease in EC (TDS) during pumping

Bromide Monitoring





Only small mass of bromide detected in Hanford Fm. at monitoring well, with the largest response at late times (final pumping campaign)



Summary: Lab/Field Geophysics and Geochemical Measurements

Component	Seismic Response	Dielectric Constant	Electrical Conductivity	Summary
HRC	Attenuates seismic response	Replacement of 10% of water filled pore space by HRC will reduce dielectric constant by 1. Attenuation will increase relative to water-filled pores.	EC increases with mixed HRC by ~20-50mS/cm.	HRC is detectable at field scale by decreased dielectric, increased radar attenuation, and increased electrical conductivity
Gases	Attenuates seismic response	Replacement of 10% of water filled pore space by gas will decrease dielectric constant by 3. Radar attenuation decreases, suggesting slight EC decrease.	Unless bubbles block all pore spaces, EC will not drop significantly.	At field scale, seismic is already attenuated from HRC. Lack of large dielectric drop and lack of decrease in radar attenuation suggests that gas bubbles not significant at field scale. This is consistent with modeling but contradicts lab-scale observations.
Mineral-ogy / Prec-ipitates	Seismic amplitude may decrease as small and dispersed ppts form and rebound as ppts aggregate.	Minor clay collapse caused by reductive processes could increase dielectric constant by 2 at longer times. Evolved precipitates could reduce porosity and decrease dielectric constant by 1.	EC decreases by 0.02 mS/cm due to clay collapse and sulfide formation. EC decrease by 0.07 mS/cm due to elemental sulfur production.	Moderate changes in dielectric and EC at later times may be associated with mineralogical and pore volume changes due to precipitate formation.
Solutes	Likely negligible, although velocity may increase as pore pressures increase	Changes in dielectric are negligible. Radar attenuation decreases as ionic strength decreases (nitrates and sulfates reduced)	EC decreases ~1.5 mS/cm per 100ppm reduction of SO4.	Reaction front evident in radar amplitudes, especially when pumped and reduction in nitrate and sulfite most prominent. Does not consider possible formation of bicarbonate as suggested by model. Geochemical measurements suggest that bromide breakthrough at down gradient well is minimal and thus is not considered as large contribution to ionic strength.

Summary

- **HRC detectable** at field scale using seismic/radar methods;
- Change in **TDS** interpreted using radar amplitudes (EC) associated with HRC and pumping (nitrate/sulfate) or minor mineralogical changes (needs verification for Hanford sediments – msmts and modeling);
- Only large early and **late bromide** peaks detected using radar attenuation (EC);
- Possible **change in mineralogy** and/or **reduction in pore space** (gas, ppts) at later times as indicated by dielectric (needs msmt/modeling verification).
- Seismic also indicates growing activity at later times in Ringold and then into Hanford – HRC, gasses, sulfide precipitates.
- **Heterogeneity** plays role in amendment distribution and system transformations;
- Lab experiments and field geochemical measurements (and modeling?) help to **reduce non-uniqueness** of geophysical signatures.

Publications/Presentations

- Hubbard et al., 12/05, AGU oral presentation
- Hubbard et al., 6/06, CMWR invited presentation
- Hubbard et al., 10/06, GSA invited presentation
- Hubbard et al. – Geophysical Characterization and Monitoring of Cr(VI) Bioreduction at the Hanford 100H Site [compared with Geochemical measurements]. Submit by Dec.
- Williams and Qusheng Jin (UCB and U of Oregon) et al. – Nature of FeS at 100H and relevance to transport and reactivity – in development.